Master's Thesis

Electrochemical polymerization of various halogenated hydrocarbons

HyunJu Nam

Department of Chemistry

Graduate School of UNIST

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HyunJu Nam

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Advisor

Rodney Scott Ruoff

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This certifies that the thesis/dissertation of HyunJu Nam is approved.

11. 27. 2018

signature

Advisor: Rodney Scott Ruoff

signature

Associate Professor: SangKyu Kwak

signature

Assistant Professor: JungMin Kee

Abstract

Diamond is highly durable, extremely hard, chemically inert, and an excellent insulator. There have been many studies to make diamond from various types of carbon precursors. For example, high temperatures and pressures are used in high pressure multi-anvil cell systems to make single crystal diamond even up to 1 cm^3 in size (this is now done by applying high temperature and pressure—HPHT growth—to inexpensive polycrystalline diamond powder (density identical or nearly so, to the single crystal diamond that will be made) and a metal catalyst like Fe or Ni), or chemical vapor deposition (CVD) growth of diamond from a hydrocarbon gas mixed with hydrogen. HPHT makes diamond pieces that are relatively small, and CVD methods produce diamond films, only. We have an interest in making diamond in new shapes, such as fibers, and others. Thus, polymers with a high concentration of sp^3-hybridized carbon are of interest to us as potentially good precursors for making diamond, including in new shapes and forms. Poly(hydridocarbyne)(PHC), which is composed of sp^3-hybridized carbon atoms, is an organic precursor that can be converted to diamond. Several methods to synthesize PHC have been reported. But there are no detailed studies reported of the structure of PHC or how it is formed—reportedly from simple molecules such as chloroform. We have made PHCs by electrochemical polymerization from several different halogenated hydrocarbons ("the monomers") and are studying how the PHC is formed in our method. In contrast to the literature reports, we now have a deeper understanding of the atomic-scale structure of PHC, its molecular weight, its density, and also whether it really only is "made from" the halogenated precursor (such as chloroform) or whether, e.g., the electrolyte is also reacting, and possible contributions from the stainless steel electrodes used in the electrolysis experiments. In a parametric study of reaction yield (and with a goal of improving yield), the influence of: (i) the electrode type and configuration, (ii) monomer and electrolyte concentration in the reaction solution, were studied. The mechanism of electrochemical polymerization has not been reported and we have explored this by varying parameters such as: the type of electrolyte, the type of solvent (and deuterated solvent), the electrode material, the type of monomer (and ^{13}C-labeled monomer) and heat-treated electrode. For scaling the synthesis to large amounts of product, we designed, tested, and built a continuous, mass production system capable of synthesizing gram-scale amounts of PHC. In the final section, I offer suggestions based on what I have learned, for possible future directions for research related to this project, such as might be conceivably done by others.

Contents

List of Figures and Tables

List of Abbreviations

DC	direct current
DMC	dimethyl carbonate
DME	dimethoxyethane
DMF	dimethylformamide
IPA	isopropanol
PET	polyethylene terephthalate
PHC	Poly(hydridocarbyne)
PI	polyimide
THF	tetrahydrofuran

1. Introduction

Diamond, the hardest material, has high chemical and electrochemical inertness and a wide band gap [1-8]. The use of various precursors to make diamond has been studied [4, 7, 9, 10]. There are now two common methods for making synthetic diamond: (i) high pressure (50-100 Kbar) and temperature (HPHT, 1500-2000 ℃) is used to produce diamond samples up to about 1 cm^3 (including single crystal) in size by recrystallization of metal-solvated carbon atoms and (ii) chemical vapor deposition (CVD, particularly PE-CVD) is used to grow (typically polycrystalline) diamond films up to about 150 mm in diameter and several microns (or more) in thickness. These two methods provide diamond in useful form for many applications. But they could never be used to make a long diamond fiber, or other shapes of diamond, and we have asked whether diamond fibers and new forms could be made, e.g., from polymers.

A method using particular polymer precursors was reported to yield diamond by heat treatment; certain polymers that have a high concentration of sp^3-hybridized carbon atoms were studied [10-16]. As these kinds of polymers can be soluble in solvents and used in a variety of established casting methods, they can in principle be processed into a wide variety of shapes, but to the best of our knowledge this has not been studied. Polymer precursors might also enable making composite materials with other substances such as doped-diamonds. It was proposed when the synthesis and structure of polycarbynes were first reported, and this has been further evaluated in other research, that it is the particular sp^3-hybridized carbon network of this class of polymers that is responsible or their thermal conversion to carbon having high sp^3 content [17-24]. The conversion of a polymer precursor, poly(hydridocarbyne) (PHC), to diamond by heating was reported in 2004 [25]. PHCs are three-dimensional polymers composed of sp^3-hybridized carbon atoms as further described below. PHC was first reported by preparation from exposure of bromoform to high intensity ultrasound in the present of NaK [25]. Due to the use of NaK the reaction must be done by scrupulously avoiding exposure to any water or oxygen which is challenging to scale up both for further fundamental studies of the product, and also commercially. In a later development, electrochemical polymerization was used to reportedly synthesize PHCs that allowed these polymers, the authors said, to be made by a simpler and quicker method involving milder reaction conditions [11, 12, 14]. They provide a stoichiometry of their PHC by elemental analysis for $(CH)_n$; C : 92.31 wt. %, H : 7.69 wt.% which yields an atomic ratio 1 : 1. However, there reports did not provide any details about either the PHC structure, or the mechanism(s) of the polymer synthesis.

Here, we report the synthesis of PHCs using our own approach to electrochemical

polymerization. Several halogenated hydrocarbons were used to produce PHCs that were then characterized with the aim to understand how the product forms and the parameters that could lead to improved yield and molecular weight. The parameters covered in this report include the type of electrolyte, the type of solvent, the type of monomer, the type of electrode material, the configuration of the electrodes, the voltage applied, and others that are described below. Isotopically labeled solvent and reagents were used where helpful in order to elucidate what contributes to the formation of PHC. For scaling the synthesis, we have designed, built, and used a continuous, mass-production system capable of synthesizing gram-scale amounts of PHC. This work continues to be the subject of ongoing research within the Ruoff group and this report covers much of our current knowledge.

2. Experiment

2.1. Materials

All reactions were carried out inside a glovebox under argon atmosphere. Anhydrous acetonitrile (99.8%), dichloromethane (≥ 99.8%), chloroform (≥ 99%, contains amylenes as stabilizer), tetrachloromethane (≥ 99.5%), and lithium hexafluorophosphate (battery grade, ≥ 99.99% trace metals basis) were purchased from Aldrich and used as received. Stainless steel 316 was purchased from KwangEun Laser cut to our desired dimensions; prior to use it was washed using acetone, IPA, and DI water with the goal of removing contaminants and dried at 80℃ in an air oven for 24 h before experiments.

2.2. Polymerization

A 6.2 M chloroform solution (in acetonitrile) was prepared in the presence of 23.0 mmol of lithium hexafluorophosphate. This solution was placed in a homebuilt vessel having a cathode and anode (each 8cm*10cm*0.1mm and stainless steel). Electrochemical polymerization was done under argon atmosphere in a glove box at 6.0V for 8h at room temperature. Direct current (DC) was used for all reactions. After the reaction, the insoluble material was removed by filtration. The filtered solution was evaporated to under reduced pressure, and the concentrated raw product was dissolved in chloroform (100mL). The solution was successively washed with diluted hydrochloric acid (100mL*5times). Finally, the chloroform was removed and afforded the desired product.

2.3. Density measurement

The density of PHC was measure using Archimedes' method. The PHC was put into hexane in a glass cylinder. Tetrachloromethane was gradually added to hexane with in intervals of 10 min to make sure the solution was well mixed. The density of this solution increases with an increasing fraction of tetrachloromethane. When the polymer suspends in the middle of the solution (doesn't sink or rise), the solution and polymer density are equal. This experiment was repeated three times to yield 1.37, 1.37, and 1.35 g/mL. As a further check we then tested two commercial polymers, polyethylene terephthalate (PET) (1.38 g/mL) and polyimide (PI) (1.42 g/mL) (densities are in parentheses—these two were obviously chosen because their reported densities are close to that obtained for our PHC). The average densities (triplicate measurement) were 1.36 g/mL and 1.42 g/mL, respectively.

2.4. Characterization

^{1}H spectra (400 MHz) of PHCs were recorded on a Bruker Ascend 400, and ^{13}C NMR (800 MHz) spectra were recorded using a Bruker Avance II 800 spectrometer equipped with a cryogenic probe at the Korea Basic Science Institute (KBSI, Ochange, Korea) by a colleague working there. ^{1}H NMR spectra were referenced with residual non-deuterated solvent shifts ($CHCl_3$ = 7.26 ppm) and ^{13}C NMR spectra were referenced by solvent chemical shift ($CHCl_3$ = 77.16 ppm). DEPT ^{13}C NMR spectra were recorded to assign carbons in the PHCs. FT-IR spectra were obtained using an Agilent 600 series spectrometer at 4 cm^{-1} resolution. IPC-MS spectra of PHC were recorded using an ELAN DRC-II at the UCRF (UNIST Central Research Facilities). Elemental analyses were performed with a Thermo Flash 2000. Gel permeation chromatography (GPC) analyses were carried out using an Agilent 1200/miniDAWN TREOS system (PLgel MIXED-C column, 5 micron, 7.5*300mm (x2), PLgel MIXED-E column, 3 micron, 7.5*300mm(x1)) equipped with UV and refractive index, multi angle light scattering (MALS) detectors (three angle). The GPC columns were eluted at a rate of 1.0ml/min with tetrahydrofuran (30 ℃). The MALS-light source is a 60mW GaAs linearly polarized laser with wavelength of 658 nm. Thermogravimetric analysis (TGA) of polymer samples were done using a TA instrument Q500 system. The TGA experiment used platinum pans and a 10℃/min ramping rate from room temperature to 900℃ in nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were done using a Thermo Scientific ESCALAB 250Xi. The gas chromatography – mass spectroscopy (GC-MS) of gas was done with a Perkin-Elmer Clarus SQ gas chromatograph with electron ionization source and a m/z 1-1200 mass analyzer.

3. Results and Discussion

3.1. Synthesis of Poly(hydridocarbyne).

The synthesis scheme of PHCs is described in **Figure 1.1**. The electrolyte ($LiPF_6$) was dissolved in solvent (acetonitrile) and the solvent has the intended function of acting as an electrical medium (later, we discuss whether the solvent might also be participating chemically in the production of the product). When we applied voltage (6V) to the solution, the polymerization initiated and proceeded at least in part by the removal of Cl atoms from the monomer ($CHCl_3$) with the formation of chlorine gas. The formation of chlorine gas was detected using Gas Chromatography – Mass Spectroscopy (GC-MS) (**Figure 1.2**). The polymer can be obtained after removing the electrolyte and residual metal "impurities" (thus, apparently some of the stainless steel electrode material enters into the solution) by washing with dilute HCl(aq). Inductively Coupled Plasma – Mass spectrometry (ICP-MS) was used to monitor the possible presence of electrolyte and metal impurities before and after the work-up process (**Table 1)**. Before work-up, the lithium and phosphorous from the electrolyte exist at a concentration of 0.74 mg/kg and 2.11 mg/kg, respectively. Iron was detected at the highest concentration in solution (6.92 mg/kg) along with other metal residues (chromium, nickel and molybdenum) and we note that these are known to be present in the stainless steel electrode. After washing the solution with diluted hydrochloric acid, most of the electrolyte could be removed.

Our primary method of synthesizing PHC was to use chloroform as a monomer. However, in chapter 3.4.1 we discuss use of two other monomers, namely PHC-CH_2Cl_2 (monomer : dichloromethane), and PHC-CCl_4 (monomer : tetrachloromethane). This method can be used with various halogenated hydrocarbons including bromoform.

$$CH_aX_b \xrightarrow[\text{Electrical current}]{\text{Solvent, Electrolyte}} [CH_2]_n + X_2$$

Figure 1.1 General reaction scheme for synthesis PHC using various types of halogenated hydrocarbons. (a, b: integer (a = 0~2, b = 4-a), n: repeating unit, X: halogen atom (Cl, Br or I))

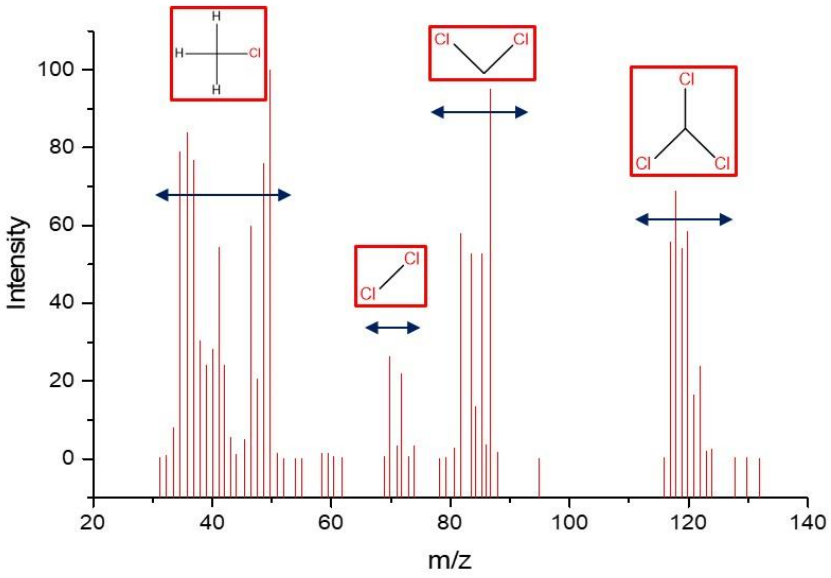


Figure 1.2 Gas chromatography – mass spectrum of gas during reaction

Table 1. ICP-MS result of metal ions before and after work-up process

Metal	Before work-up process Concentration (mg/kg)	After work-up process Concentration (mg/kg)
Li	0.74	0.001
P	2.11	0.000
Fe	6.92	0.003
Mo	5.45	0.007
Cr	1.68	0.009
Ni	0.89	0.000

3.2. Characterization of Poly(hydridocarbyne).

3.2.1. Structure analysis

It should be noted that I, in the following sections, refer to the product material as "PHC" and this is, frankly, in part "a convenience." The detailed structure of PHC has never really been published, to the best of our knowledge. The name has been used in a number of papers including the discovery paper in 2004 [25]. PHCs were investigated using ^{1}H and ^{13}C NMR, and FT-IR, spectroscopies, by XPS, and by elemental analysis (EA). To investigate the molecular structure and explore the possible formation of PHC, we collected ^{1}H and DEPT (Distortionless Enhancement by Polarization Transfer) ^{13}C NMR spectra of PHC. The ^{1}H NMR spectrum (**Figure 2.1a**) shows three peaks located at 1.59ppm, 1.25 ppm and 0.88 ppm that are assigned as -CH, -CH_2 and -CH_3 groups, respectively. Compared with the monomers or simple organic compounds, the NMR spectrum of polymers show relatively broad peaks and thus peaks having similar positions are overlapped. This makes it difficult to acquire detailed information about molecular structure from ^{1}H-NMR alone. Thus the molecular structure of PHC was also analyzed by DEPT-^{13}C-NMR (**Figure 2.2**). In a DEPT ^{13}C-NMR experiment, a sequence of pulses with different delay times are used to record the spectra. DEPT-90 yields only CH signals, DEPT-135 yields positive peaks for CH and CH_3 while the CH_2 peak is negative [26]. Based on DEPT ^{13}C-NMR spectra, the fraction of -CH, -CH_2 and -CH_3 groups were calculated as 0.56 (-CH) : 2.17 (-CH_2) : 1 (-CH_3) which correlates with an empirical formula of –$(CH_{2.12})_n$–. FT-IR spectrum of PHC is shown in **Figure 2.1b**. The observed strong band in the range of 2855 cm^{-1} to 2925 cm^{-1} can be assigned as C-H stretching [27, 28]. The C-H scissoring peaks appear at 1458 cm^{-1} and 1375 cm^{-1} [27, 28]. The absence of C=C related bands (typically observed between 1640 cm^{-1} and 1670 cm^{-1}) supports the formation of a fully sp^3 carbon network structure.

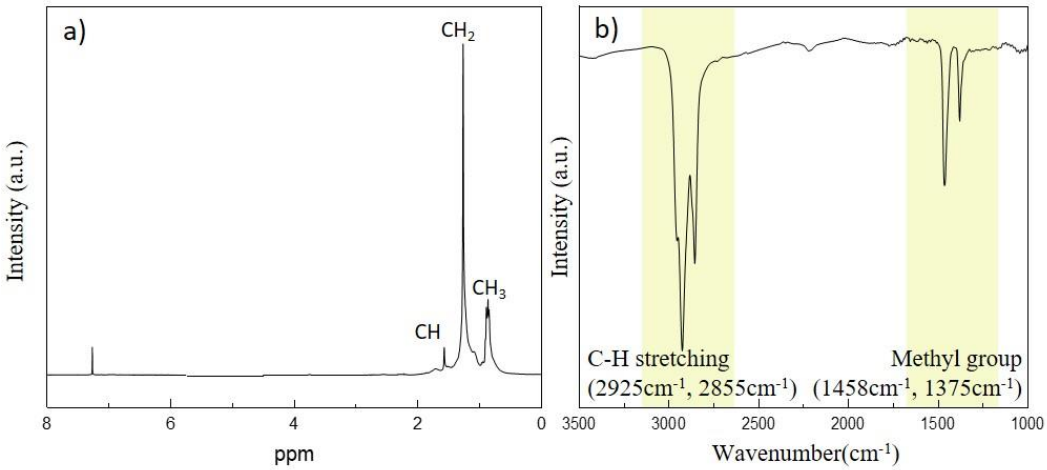


Figure 2.1 a) ^{1}H NMR spectra of PHC in $CDCl_3$ and b) Transmission IR spectra of PHC.

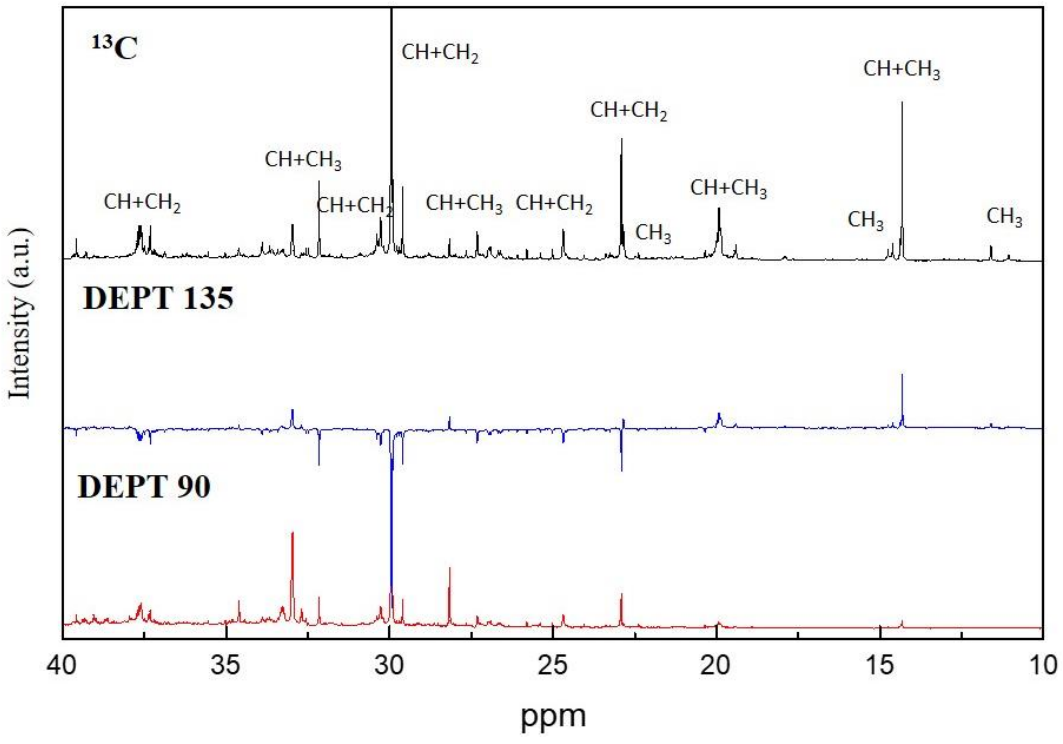


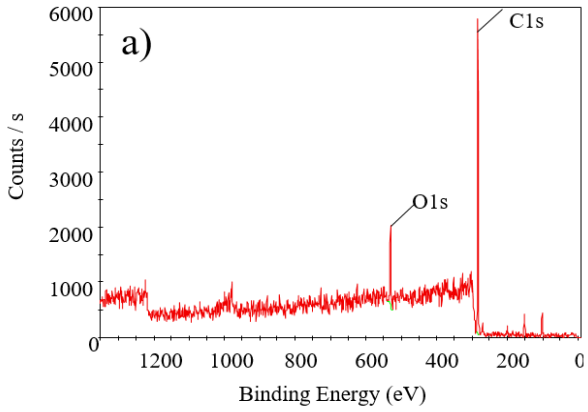
Figure 2.2 ^{13}C NMR and DEPT spectra of PHC

Elemental analysis (EA) and X-ray photoelectron spectroscopy (XPS) were also used to investigate the elemental composition of PHC. The atomic percent of carbon, hydrogen, nitrogen and oxygen atoms was measured using elemental analysis with the combustion method (**Table 2**). The observed small amount of nitrogen and oxygen probably stems from gas, water, or solvents trapped inside the material. According to EA, the empirical formula of PHC was calculated as $–(CH_{1.84})_n–$ which differs somewhat from the formula $–(CH_{2.12})_n–$ obtained using DEPT ^{13}C NMR.

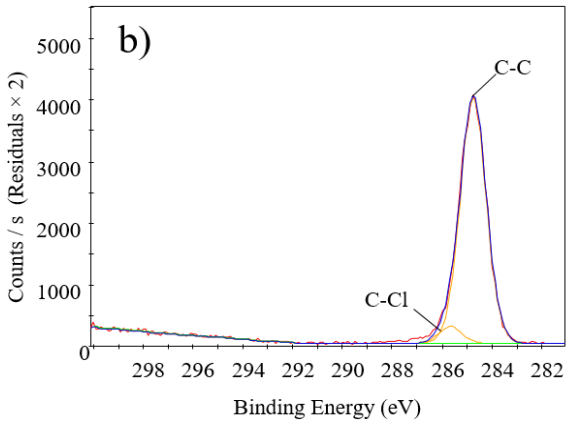
Table 2. Elemental analysis of PHC (at.%)

Carbon	Hydrogen	Nitrogen	Oxygen	X (CHx)
34.89	64.40	0.09	0.61	1.84

XPS survey analysis shows 1.1 at.% of chlorine along with 7.85 at.% of oxygen (**Figure 2.3a**). The small amount of chlorine atoms are probably due to the unreacted end groups that are likely on the periphery of the polymer molecules. The high-resolution C1s spectrum of PHC (**Figure 2.3b**) had two overlapped peaks. The strong signal at ~284.8 eV was assigned to sp^3 hybridized carbon atoms, with the smaller contribution at 286.2 eV thought to arise from C-Cl bonds [29, 30]. According to this high-resolution C1s spectrum, the carbon in PHC is composed of 98.25% sp^3 carbon.



Name	Peak BE	FWHM(eV)	Atomic %
C1s	285.28	1.18	91.05
O1s	530.36	1.53	7.85
Cl2p	199.48	1.44	1.1



Name	Peak BE	FWHM(eV)	Atomic %
C-C	284.8	1.19	98.25
C-Cl	286	0.43	1.75

Figure 2.3 XPS spectrum with integral tables of PHC. a) Survey scans and b) high resolution C1s Scan

PHC was determined to be a macromolecular species by Gel Permeation Chromatography with Multi-Angle Light Scattering (GPC-MALS) and Transmission Electron Microscopy (TEM). For dendritic polymers, GPC measurements often produce much smaller M_w values due to the poor performance of polystyrenes as calibration standards [31]. Therefore, we measured the molecular weight of PHCs using a multi-angle light scattering detector. The molecular weight was 1.67 * 10^5 Da with polydispersity index (PDI) of 1.45 and a refractive index increment (dn/dc) of 0.084 mL/g. The dn/dc value was measure manually each time in our use of GPC-MALS rather than using a reference value. Although other techniques that can sometimes allow determination of the "true" molecular weight of certain polymers, such as MALDI-TOF (Matrix-Assisted Laser Desorption/Ionization Time-Of Flight), DART (Direct Analysis in Real Time) and ESI (Electrospray Ionization), when we used these methods with PHC, and at least in the way that we employed them, they did not allow determination of the MW of PHC.

The morphology of PHCs was studied by Transmission Electron Microscopy (**Figure 2.4**). The TEM sample was prepared by coating PHC diluted in THF onto a carbon mesh grid (with monolayer graphene as the support layer). The PHC particles were found by TEM to have a globular shape with an average diameter of ~30 nm.

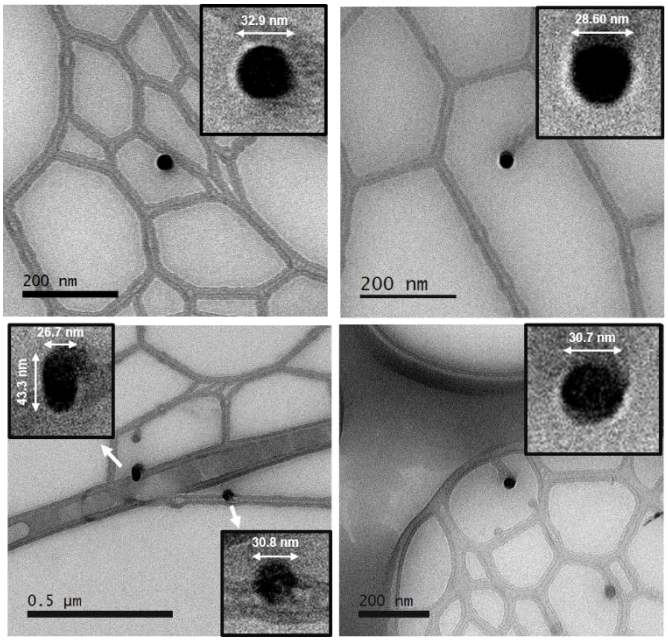


Figure 2.4 TEM image using single electron detector at 200 keV, exposure time: 2.0 s

3.2.2. Property study of PHCs

It is very important to know various properties of PHC for fundamental understanding as well as for its potential use, including in making composites with other materials or fabricating fibers or films, for 3D fabrication, and so on, using PHC. To the best of my knowledge there have not been any studies about the properties of PHC until our work reported here. We studied its thermal stability, solubility in some solvents, and density, as described below.

(i) Thermal Stability

- The thermal stability of PHC was investigated using Thermogravimetric analysis (TGA). TGA of PHC showed it is stable up to 150 ℃ in N_2 atmosphere and gradually decomposes when the temperature is increased to 900 ℃ (**Figure 2.5**). The residual mass after heating to 900℃ was 21.65 wt.%. While both high-density and low-density polyethylene totally decomposed at around 500 ℃ and left no residue [32], PHC yields more carbon residue and this could be due to its relatively high molecular weight and sp^3 carbon backbone structure.

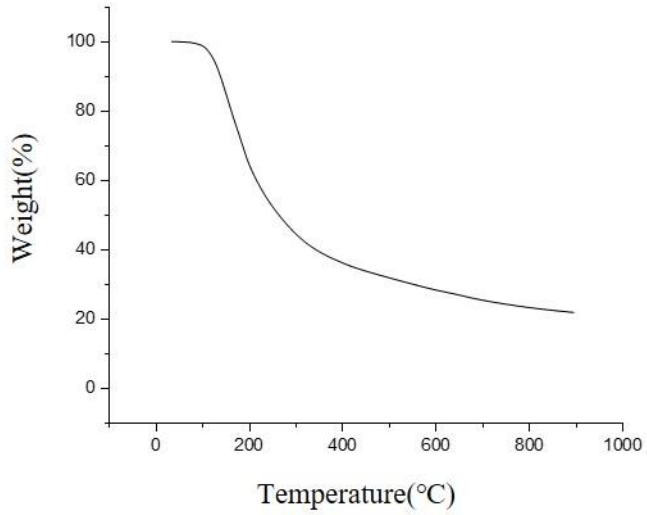


Figure 2.5 Thermogravimetric analysis (TGA) curve for PHC under N_2 atmosphere heated from 25 °C to 900 °C with a ramping rate 10 °C /min

(ii) Solubility Tests

- We chose seven solvents in our study of the room temperature solubility of PHC. Dimethyformamide (DMF), tetrahydrofuran (THF), ethanol, isopropanol (IPA), acetonitrile, toluene, and n-hexane (**Table 3**). An excess of PHC was placed in each solvent and sonicated for 10min such that a saturated solution was obtained; the undissolved PHC was removed by filtering through a syringe filter (0.2 um). The room temperature solubility was then found by drying and then weighing the remaining PHC, and in DMF and THF it was 79.5 mg/mL and 77.1 mg/mL, respectively, but was 5.7 mg/mL in n-hexane. Thus at room temperature PHC can be well dissolved in several common polar solvents.

Table 3. Solubility test of PHC in seven common solvents

Entry	Solvent	Solubility (mg/mL)	Polarity
1	DMF	79.45	13.7
2	THF	77.10	5.7
3	Ethanol	34.25	8.8
4	IPA	19.15	6.1
5	Acetonitrile	18.70	18
6	Toluene	8.55	1.4
7	n-hexane	5.65	0

(iii) Density measurement

- To measure the density by Archimedes' principle two miscible solvents should be chosen with one having a lower density and the other a higher density then the material of interest. When sample is placed in the lower density solvent it sinks to the bottom. As the higher density solvent is gradually added in known amounts the sample eventually rises to the middle of the solution due to equal density. For our experiment, tetrachloromethane and n-hexane were used as the high and low density solvents, with density of 1.59 g/mL and 0.655 g/mL, respectively. The experiment was repeated three times and the average value was 1.36 g/mL (**Table 5**).

- As a check after determining the density of PHC by this method, we did a control experiment with PET (polyethylene terephthalate) and PI (polyimide) as standards with known densities reported to be near the value we obtained for our PHC (**Table 4**). The reference density of PET is 1.38 g/mL, and our average value by this experiment was 1.37 g/mL. The reference density of PI is 1.42 g/mL, and we obtained 1.43 g/mL.

Table 4. Density measurement of PET (polyethylene terephthalate) and PI (polyimide)

Entry	Solvent	Density(g/mL)	PET (density: 1.38g/mL)		PI (density: 1.42g/mL)	
			Volume(ul)	Calculated Density(g/mL)	Volume(ul)	Calculated Density(g/mL)
1	CCl_4	1.59	4000	1.36	8800	1.42
	Hexane	0.655	1320		1900	
2	CCl_4	1.59	2000	1.37	4000	1.43
	Hexane	0.655	600		850	
3	CCl_4	1.59	1500	1.36	2000	1.44
	Hexane	0.655	480		480	
			Average	1.37	Average	1.43

Table 5. Density measurement of PHC

Entry	Solvent	Density(g/mL)	Volume(ul)	Calculated Density(g/mL)
1	CCl_4	1.59	4800	1.37
	Hexane	0.655	1500	
2	CCl_4	1.59	3150	1.37
	Hexane	0.655	1000	
3	CCl_4	1.59	2850	1.35
	Hexane	0.655	1000	
			Average	1.36

(iv) Atomic scale structure model study

- Based on our analysis and study of PHC, we "sketched out" a PHC structure and calculated the number of each of the elements (C, H, and Cl) with some assumptions (with the goal of obtaining, for example, a "geometric" model that could be tested against the measured amount of Cl, and so on). For convenience, we supposed our polymer is a perfect sphere with diameter of 30 nm, since this was the diameter observed with TEM (of course, it might be a flattened sphere like a disc…but for the sake of having a well defined model, we here assume a sphere). Additionally, we assume the Cl atoms exist only at the surface of this polymer because we don't detect Cl near H (shown around 3~4 ppm in ^{1}H NMR), but Cl is detected with XPS. For calculating the number of Cl atoms on the surface and $(CH_2)_n$ atoms in the interior, we used the surface area of this 30 nm-diameter sphere and also its volume, respectively. In calculation of the "interior space", the radius of the methylene ($-CH_2$) group was calculated with bonding angle of C-H (109 °) and bond length C-H (0.109 nm).

- The number of Cl atoms at the surface was obtained as the *surface area of the polymer particle* divided by *the cross sectional area of chlorine atoms*.

  ✓ Surface area of PHC molecule : $4\pi * (15nm)^2$

  ✓ The cross section area of chlorine atom : $\pi * (0.175nm)^2$

  ✓ The number of chlorine atom at surface : $\frac{\mathbf{4\pi(15nm)^2 * \alpha}}{\mathbf{\pi(0.175nm)^2}}$ (α : packing factor)

- The number of $-CH_2$ groups in the interior is obtained as *volume of the polymer* divided by *volume of -CH_2 groups*.

  ✓ Volume of PHC molecule : $\frac{4}{3}\pi * (15\text{nm})^3$

  ✓ Radius of CH_2 group : $2 * 0.109 * \sin\frac{109^\circ}{2}$ = **0.177nm**

  ✓ Volume of CH_2 group : $\frac{4}{3}\pi * (0.177\text{nm})^3$

  ✓ The number of CH_2 group in inner space : $\frac{\frac{4}{3}\boldsymbol{\pi * (15nm)^3 * \alpha}}{\frac{4}{3}\boldsymbol{\pi * (0.177nm)^3}}$ (α : packing factor)

- Finally, we obtained the fraction of Cl atoms in the PHC molecule as *the number of Cl atoms* divided by *the number of -CH_2 groups*, per this model. The calculated at% of Cl is 1.2%. This can be compared with the XPS result of 1.1% in **Figure 2.3**. We also calculated the MW using an assumed sphere of 30 nm diameter with density 1.38 g/mL and formula CH_2, see below for details. The value obtained is 8.37 * 10^5 Da, in reasonable agreement with 1.67 * 10^5 Da obtained by GPC-MALS.

  - ✓ $Weight = Density * Volume$
  - ✓ Density : 1.38 g/cm^3
  - ✓ Volume of PHC molecule : $\frac{4}{3}\pi * (15\text{nm})^3$
  - ✓ Molar Mass of –CH_2 group : 14 g/mole
  - ✓ Weight of PHC molecule : $1.38\text{g}/cm^3 * \frac{4}{3}\pi * (15\text{nm})^3 * \frac{1}{14g/mol} * 6.023 * 10^{23}$
  - ✓ Molecular weight : 8.4 * 10^5 Da

- The summary of this calculation with MW of 8.37*10^5 Da is shown in **Table 6**.

Table 6. Actual number of atoms result of calculation

	C	H	Cl
Molar Mass	12	1	35.5
Subtotal mass (%)	32.6	65.2	2.2
Subtotal mass (g/mol)	391.2	65.2	78.1
Mass percent (%)	73.19	12.20	14.61
Weight mass (g/mol)	612600	102114	122285
Number of atoms	**51050**	**102114**	**3445**

3.3. Study of parameters related to synthesis of PHC

In chemical synthesis, obtaining a high yield is essential for scaling up a reaction. In order to optimize our reaction conditions to obtain higher yields, different reaction parameters were tested. First of all, we explored the role of monomer and electrolyte concentration on the electrochemical polymerization (**Table 7**). The highest yield was obtained when the volume ratio of monomer to solvent was 0.5 (Entry 2). When we analyzed the effect of monomer concentration on polymerization, we found that an increase of monomer concentration leads to an increase in the yield, up to a volume ratio of 0.5 (Entry 1 to 3). Monomer concentrations above this 0.5 ratio decreased yield. We suggest this might be due to the monomer reducing the solubility of the electrolyte in the reaction mixture; a reduced solubility of the electrolyte increases solution resistance, and the current is likely too low for polymerization to proceed. In the case of varying the electrolyte concentration, increasing the concentration beyond 23mM does not improve the reaction yield (Entry 2, 4, and 5). We attribute this to the electronic current density being saturated. Based on these results, we optimized our yield as per entry 2.

Table 7. Effect of different concentration of monomer and electrolyte to reaction yield

Entry	Monomer (mL)	Solvent (mL)	Volume ratio (monomer/solvent)	Electrolyte(g)	Yield (mg)
1	50	250	0.2	0.70 (23mM)	35
2	100	200	0.5	0.70 (23mM)	119
3	200	100	2	0.70 (23mM)	3
4	100	200	0.5	0.10 (0.3mM)	13
5	100	200	0.5	1.40 (46mM)	105

Besides the effect of monomer and electrolyte concentration, we considered the configuration of the cell electrode (**Table 8**). We found that increasing the distance between the cathode and anode results in a decrease in the yield due to a decrease in the resistance of the solution (Entry 1 to 3). We also found that the electrode surface area does not significantly affect the reaction yield (Entry 3 to 5).

Table 8. Effect of different electrode configuration to reaction yield

Entry	Distance between cathode and anode	Surface Area (cm^2)	Yield (mg)
1	2.5cm	24	121mg
2	5cm	24	61mg
3	10cm	24	21mg
4	10cm	48	17mg
5	10cm	8	15mg

After optimizing the reaction conditions per the aforementioned parametric studies, we investigated the effect of reaction time on the PHC MW. We used GPC-MALS to determine the MW of the resulting PHCs (**Figure 3.1**). We found an increase in the MW with reaction time for reaction times up to about 24 hours, but for times longer than 24 hours there was no significant change in the MW.

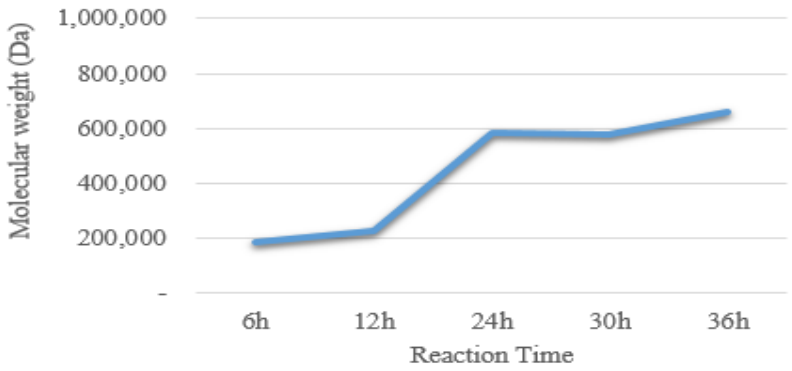


Figure 3.1 Molecular weight of PHC depending on reaction time.

The production of large amounts of PHC could be achieved by scaling up the reaction. While the experimental setup of electrochemical polymerization probably allows for straightforward industrial scale up, the constraints of the equipment available in a laboratory setting makes this difficult. So, we designed, tested, and used a continuous flow reaction system that uses a peristaltic pump for solution flow. The schematic is shown in **Figure 3.3**. At each of the junctions for the product and solution, a three-way valve was installed. In this manner, the reaction could be divided into three steps by changing the configuration of the valves, namely *monomer loading* (**Figure 3.3a**), *electrochemical reaction* (**Figure 3.3b**), and *product separation* (**Figure 3.3c**). In this experimental configuration we achieved homogenous mixing, as well as automated monomer loading and product separation. This allows the polymerization to run continuously without intervention. We made a large plastic glove box for this automated mass production system (**Figure 3.2**). We routinely use this system to produce gram scale quantities of PHC that are needed for a variety of experiments including fiber spinning, making composites with diamond powder, and others.

Figure 3.2 Photo of continuous mass production

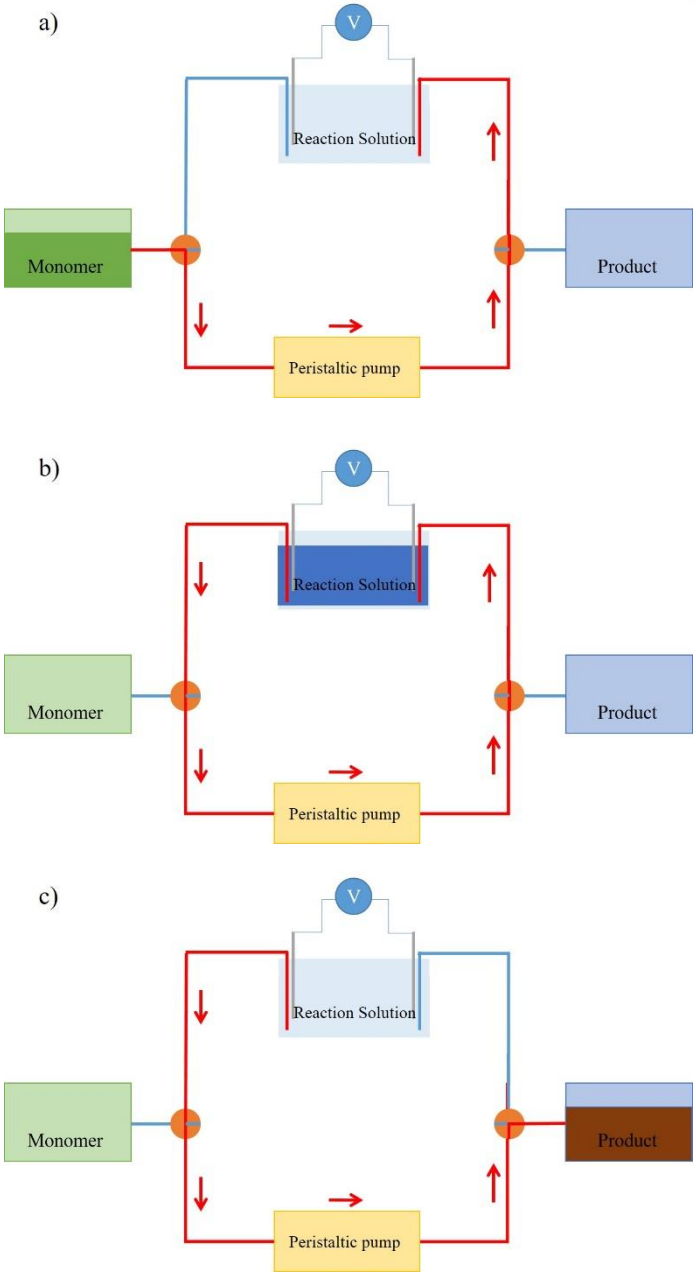


Figure 3.3 Schemes of continuous mass production system.

a) Put monomer in to reaction batch

b) Homogenous mixing solution through continuous flow

c) Bring product out from reaction batch

3.4. Reaction mechanism study

To study reaction mechanism(s), we changed various parameters such as the types of monomer, solvent and electrode material.

3.4.1. Change of monomers

To explore whether different monomers could be used to make PHC, we considered; (i) PHC-CH_2Cl_2 (monomer: dichloromethane, (ii) PHC-$CHCl_3$(monomer: chloroform) and (iii) PHC-CCl_4 (monomer: tetrachloromethane). CH_2Cl_2 can be considered as having one less reaction site than $CHCl_3$, while CCl_4 can be considered as having one more. We characterized the products using ^1H NMR and FT-IR spectrum. In ^1H NMR analysis, as seen in the **Figure 4.1a**, all products show same the resonance peak at 1.59ppm, 1.25ppm and 0.88ppm which corresponding to the -CH, -CH_2 and -CH_3 groups in PHC, respectively. Additionally, the presence of C-H groups was verified using FT-IR spectroscopy (**Figure 4.1b**). The signal observed in the range from 2855 cm^{-1} to 2925 cm^{-1} and 1458cm^{-1} and 1375cm^{-1} are due to C-H stretching and bending, respectively.

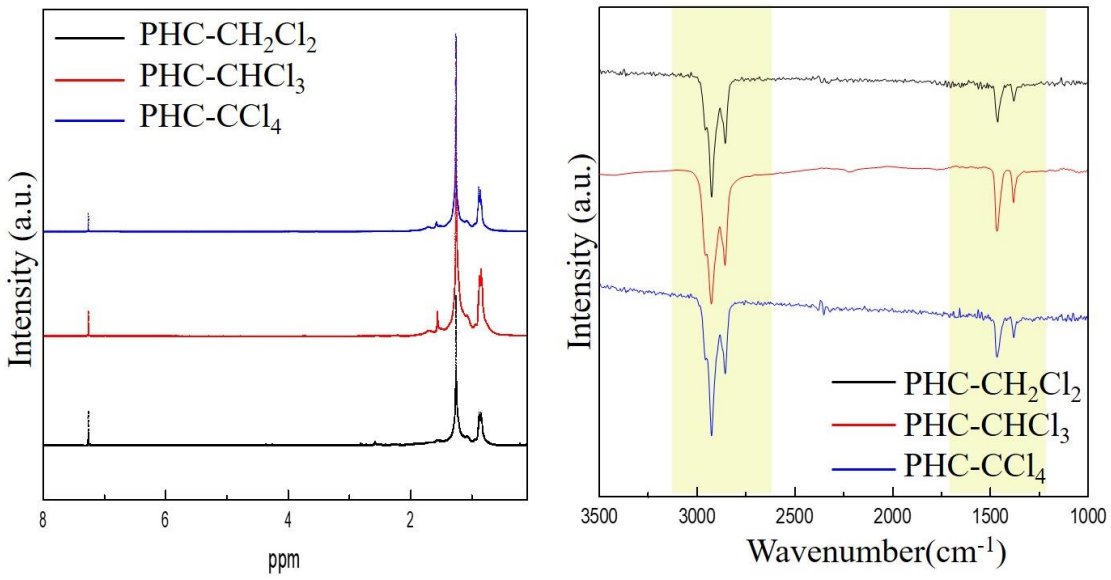


Figure 4.1 a) ^1H NMR spectra comparison using different types of monomer b) Transmission IR spectrum comparison using different types of monomer (Black: Dichloromethane, Red: Trichloromethane, Blue: Tetrachloromethane)

We found that using these three different monomers led to changes in thermal stability, stoichiometry, molecular weight, and yield of the resulting products, which we do identify as PHCs. We found that there was significant increase in both the yield and MW for PHC-CCl_4 compared with PHC-$CHCl_3$ and PHC-CH_2Cl_2 (**Table 9**). The PHC-CCl_4 shows four times higher yield and seven times higher MW than PHC-CH_2Cl_2. This result can be interpreted as: the removal of the Cl results in a reaction site for polymerization, and an increase in the number of sites for polymerization gives a higher yield.

Table 9. Yield and molecular weight of PHC using different types of monomer

Monomer	Yield	Mw(g/mol)	PDI
CH_2Cl_2	50~70mg	$7.742*10^4$	1.169
$CHCl_3$	150~200mg	$1.675*10^5$	1.446
CCl_4	200~250mg	$5.689*10^5$	1.311

The TGA for the PHC products from these 3 monomers is shown in **Figure 4.2**. After heat treatment to 900°C, the remaining residues totaled 14.9% for PHC-CH_2Cl_2, 21.6% for PHC-$CHCl_3$ and 29.6% of PHC-CCl_4. In addition to the MW, the concentrations of C and H in the respective product PHCs could contribute to the differences in TGA data (**Table 10**).

Table 10. Elemental analysis of PHC using different types of monomer (at.%)

Monomer	Carbon	Hydrogen	Nitrogen	Oxygen	X (CHx)
CH_2Cl_2	34.91	64.58	0.00	0.51	1.85
$CHCl_3$	34.89	64.40	0.09	0.61	1.84
CCl_4	36.53	62.09	0.55	0.83	1.69

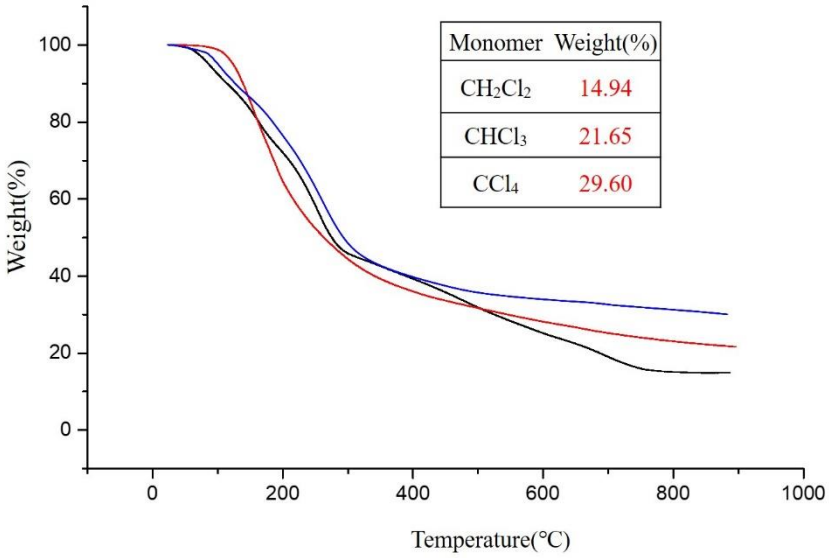


Figure 4.2 Thermogravimetric graph from room temperature to 900℃ in N_2 atmosphere, ramping rate: 10℃/min. (Black: Dichloromethane, Red: Trichloromethane, Blue: Tetrachloromethane)

3.4.2. Trying to find out the source of hydrogen atoms

^{1}H-NMR, ^{13}C-NMR, and elemental analysis (EA) show that all PHCs have a 'hydrogen rich' polymeric backbone. Even PHC-CCl_4 prepared from a hydrogen free monomer has a hydrogen content up to 62.08 at. % based on EA. Are there possible hydrogen sources other than the monomers? We identified three possible sources hydrogen.

(i) Moisture (from the surrounding environment)

- Although synthesis was done in a glove box with anhydrous solvent, there could be water from the environment 'contaminating' the experiment. We deliberately added known amounts of water to see its influence. As soon 50ul of H_2O was added the current rapidly dropped to zero and the reaction stopped. We suggest:

$$LiPF_6 \rightleftharpoons Li^+ + PF_6^- \quad (1)$$

$$LiPF_6 \rightleftharpoons LiF + PF_5 \quad (2)$$

$$PF_5 + H_2O \longrightarrow POF_3 + 2HF \quad (3)$$

That is, the hydrolysis of electrolyte ($LiPF_6$) "kills" the reaction. When $LiPF_6$ is dissolved in acetonitrile it dissociates into its ions thus establishes chemical equilibrium with its molecular dissociation products LiF and PF_5 (eq1, 2) [33-35]. It is hydrolyzing faster in organic solutions when water is added by generating HF (eq 3) [33]. We conclude that water cannot be a source of H atoms in our reaction.

(ii) Solvent (acetonitrile)

- We examined possible additional sources of H atoms by ^{1}H NMR spectrum using combinations of deuterated solvent and/or deuterated monomer, specifically studying the one monomer $CDCl_3$, **(Figure 4.3)**. The four experiments were: a) AN(H)+$CHCl_3$, b) AN-d_3+$CHCl_3$, c) AN(H)+$CDCl_3$ and d) AN-d_3+$CDCl_3$. The same amount and concentration of sample was prepared, and the integrated peak areas were compared. The ratio of the area of the PHC peak region (0.8~1.6 ppm) to the residual non-deuterated solvent ($CHCl_3$ = 7.26 ppm) is shown in **Table 11**. The intensity of the peak in **Figure 4.3c** decreased significantly from **Figure 4.3a** and we could thus conclude that most of the hydrogen in the polymer is generated from the hydrogen present in the chloroform.

However, when we change the solvent to a deuterated solvent (**Figure 4.3b**), the intensity of the peak also decreased from **Figure 4.3a** which indicating that solvent also contributes hydrogen. We note that it is important to know that H atoms are generated from not only the monomer but also the solvent. In short, there is not only one reactant, the monomer, but the solvent is both a solvent as well as a chemical reactant. (Others have not reported whether the solvent in their production of PHC, was playing a chemical role, or not.)

Activation of the of C-H bonds in acetonitrile has been studied under 'harsh' conditions as well as in the presence of catalyst (Nickel or CpRu complex, DBU and $NaPF_6$) [36-38]. A yellowish polymer above a pressure of 1.7 GPa was said to be the result of a hydrogen transfer reaction [38]. To further examine the role played by acetonitrile we ran the reaction with only acetonitrile present, i.e., without monomer. The transmission IR spectrum of this yellowish product is shown in **Figure 4.4**. The spectrum has intense band at 3417 cm^{-1}, 1558 cm^{-1} which arises from primary amine group with C≡N group at 2221 cm^{-1}. Therefore, the product of electrochemical reaction using only acetonitrile composed of amine group and nitrile group which result of hydrogen transfer reaction. Even though the detailed reaction pathway(s) involving acetonitrile and halogenated monomer that lead to PHC is(are) not yet known, acetonitrile certainly seems to be contributing to the product through the donation of H atoms.

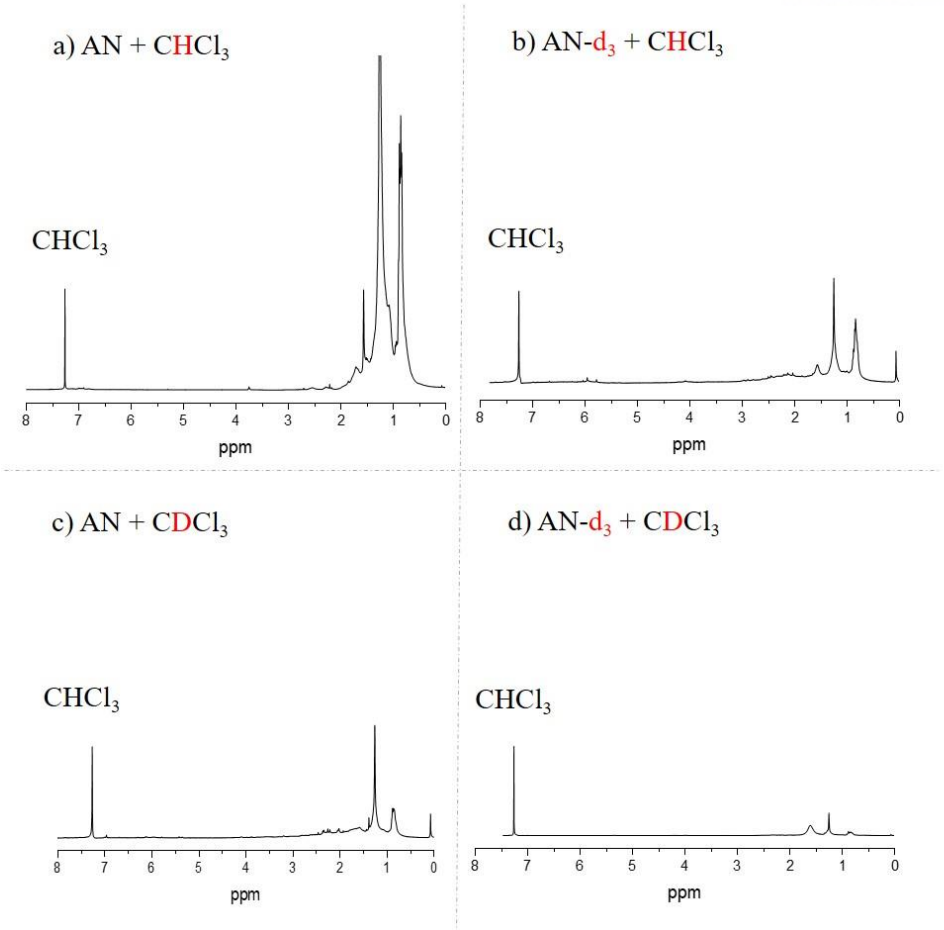


Figure 4.3 ^{1}H NMR spectrum of PHC using deuterium solvent.

a) acetonitrile (H), chloroform (H), b) acetonitrile (D), chloroform (H),

c) acetonitrile (H), chloroform (D), d) acetonitrile (D), chloroform (D).

Table 11. Integration value comparison of four entry

Experiment	Peak Area
(a) AN + $CHCl_3$	184
(b) AN-d_3 + $CHCl_3$	13.45
(c) AN + $CDCl_3$	11.8
(d) AN-d_3 + $CDCl_3$	2.8

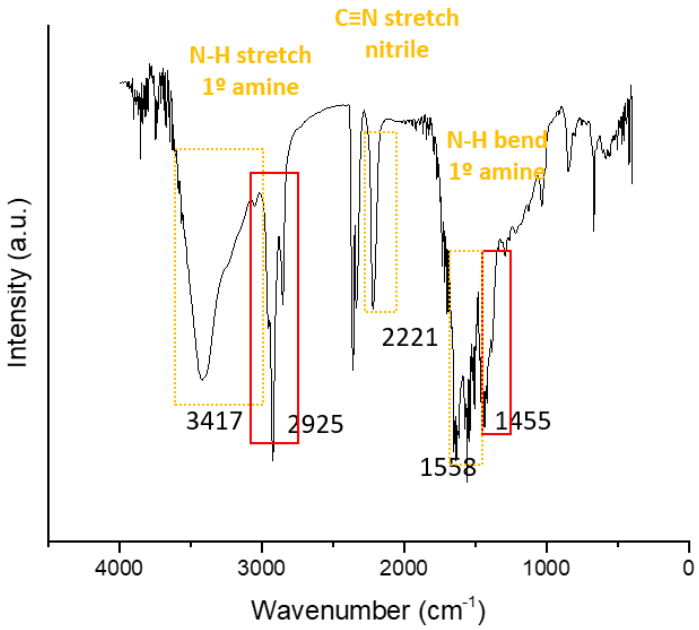


Figure 4.4 Transmission IR spectrum of polymerization using acetonitrile only. (Red Box : CH functional group of PHC)

(iii) Electrode (Stainless Steel)

- We also considered the possible contribution(s) of hydrogen atoms that might be present in the stainless steel electrodes. It is well known that hydrogen can dissolve in metals, including stainless steel [39]. In an attempt to remove hydrogen that might possibly be present on the surface of the stainless steel foils that are our electrodes, I heated them under an Ar atmosphere for 5 days at 500°C. The deuterated solvents (acetonitrile and chloroform) were used to try to see if H might be coming from the electrodes. Two experiment were run, one with the heat-treated electrodes (cathode and anode) and another the non-heat treated electrodes (cathode and anode). ^{1}H NMR was done on the solutions following these experiments (**Figure 4.5**). However, whether we used heat-treated electrode or non-heat-treated electrode, there is no significant difference between intensity of peak (the number of H atoms).

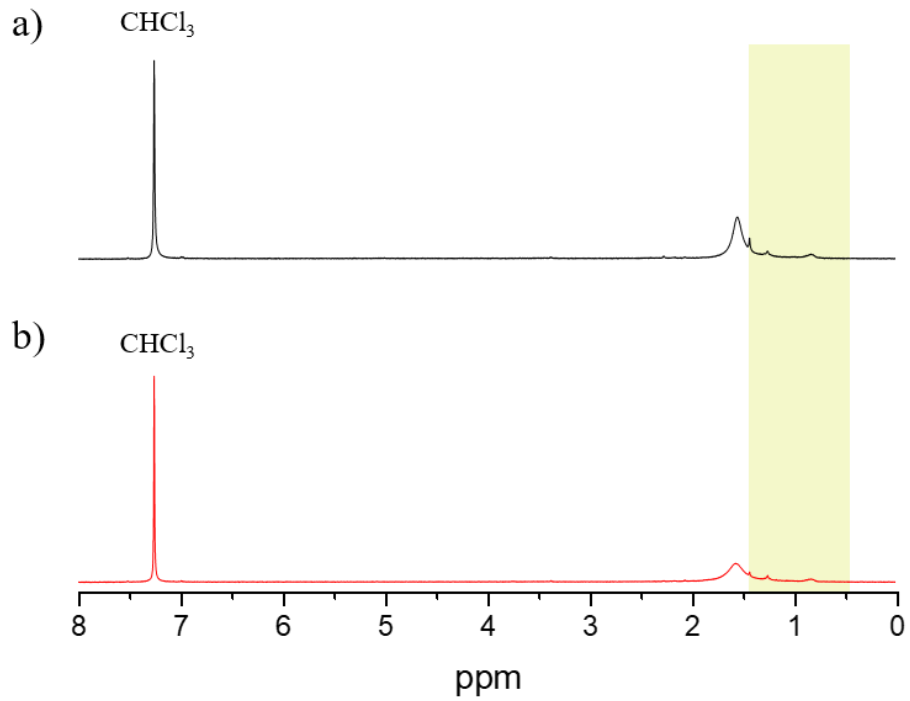


Figure 4.5. ^{1}H NMR spectra of PHC a) with heat treated electrode b) with non-heat treated electrode

3.4.3. Effect of solvent type

Based on all of our studies (chapter 3.4.1 and 3.4.2), one reaction site is the C-Cl bond in the monomer and acetonitrile also participates by donating one or more H atoms during the polymerization. We thus tested 3 other solvents; dimethyl carbonate (DMC), dimethoxyethane (DME) and dimethylformamide (DMF) instead of acetonitrile with chloroform as monomer. No product was found from the use of dimethyl carbonate or dimethoxyethane. DMF did yield PHC, however with lower yield than acetonitrile.

The PHC produced from DMF was studied by ^{1}H-NMR, and FT-IR, spectroscopy (**Figure 4.6**). The ^{1}H NMR spectrum shows three peaks at 1.59 ppm, 1.25 ppm, and 0.88 ppm that are assigned as -CH, -CH_2, and -CH_3 groups, respectively. In the FT-IR spectrum, the unexpected peak positions are observed (at least, that we might expect for PHC from the studies using acetonitrile as the solvent) along with residual DMF peaks at 1656 cm^{-1}. The polymer that is produced by using DMF rather than AN will be further studied.

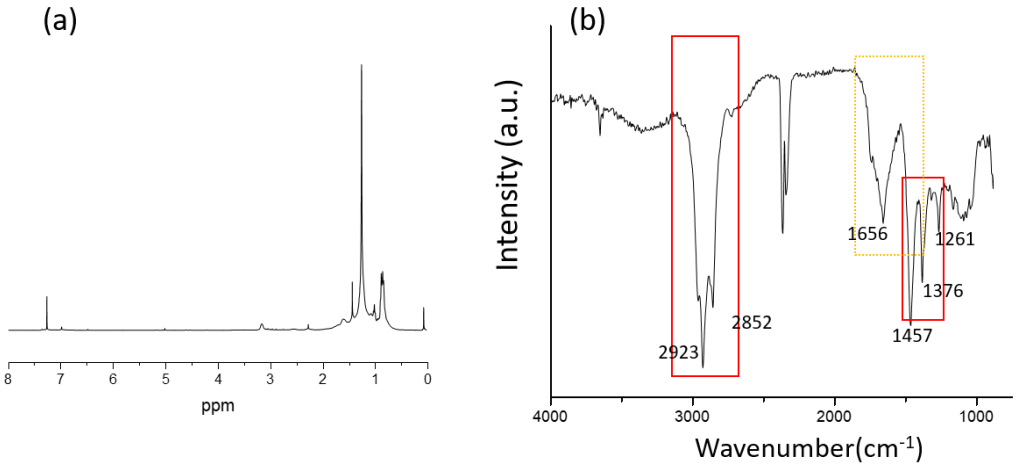


Figure 4.6 a) ^{1}H NMR spectra of PHC using DMF as solvent and b) Transmission IR spectrum of PHC using DMF as solvent (Red Box : CH functional group of PHC)

3.4.4. Effect of electrode

To further examine the possible role of the stainless steel electrodes, other electrode materials were tested: platinum, copper, brass, and iron, instead of stainless steel. From the ICP-MS result **(Table 1**), we can see that various metals exist in the reaction solution. These might contribute to the formation, or inhibit formation, of PHC, for example, by reductive dechlorination of the monomer [40, 41]. We plan to test electrodes consisting only of the pure metal for those metal impurities that were identified as being present in the reaction solution after use of the stainless steel electrode (Cr and Ni were predominant). We also will test further by adding certain metal salts to the solution, but in that case using a platinum electrode rather than stainless steel.

4. Conclusion

The "poly(hydridocarbyne)" that has been identified in several published papers as a precursor for diamond was synthesized and its chemical formula and some aspects of how it is formed from each of the monomers CH_2Cl_2, $CHCl_3$, and CCl_4, was studied. PHC contains -CH, -CH_2, and -CH_3 groups in the ratio 0.5 : 2 : 1 from DEPT-NMR. The PHCs I made consist of sp^3–bonded carbon with stoichiometry of –($CH_{1.84}$)– determined by ^{13}C-NMR, and –($CH_{2.12}$)– by EA. The MW of PHCs measured using GPC-MALS and my study of the dependence on reaction time showed that MW increases for reactions conducted up to 24 hours but for longer times the MW is essentially constant. Thermal stability was studied with TGA and density measured by Archimedes' method.

With an aim of maximizing yield, some reaction parameters were tested such as concentration and type of monomer, solvent, and electrolyte, and the configuration of the stainless steel electrodes.

The reaction was also studied in terms of several parameters and I learned that: CCl_4 resulted in higher yield, molecular weight, and C:H ratio, than $CHCl_3$, and in turn, CH_2Cl_2, The source of H atoms was studied with deuterated vs normal solvents and by also trying to figure out if the ss electrodes were possibly contributing H atoms . We thereby learned in a study with $CHCl_3$ as the monomer that both the acetonitrile (nominally, the "solvent") and the $CHCl_3$ are contributing H to the product PHC. Thus, the solvent is, here, not a pure solvent—it is participating in the reaction. Further studies of the possible contribution of the electrode (e.g., the ss electrodes are evidently contributing metal ions such as Cr, Ni, and others and further studies of the role of the "solvent" and electrode (its material composition, possible role of these dissolved ions that come from the electrode at 6V, and so on) are needed.

Finally, we designed, built, tested, and used a continuous, 'mass-production' system that readily produces gram-scale quantities of PHC.

5. Suggestions for further research

Further studies are clearly needed about the effect of the solvent type and its role in the chemistry occurring, as well as that of the electrode material—and as seen, I obtained very interesting results as a function of the chlorinated methane used. Polymerization occurs with acetonitrile or dimethylformamide (DMF) as solvent but not dimethyl carbonate (DMC) or dimethoxyethane (DME). Why? We don't yet know. We noted that the product color was dark green with DMF as solvent but brown with acetonitrile as solvent, and the same brown color was seen in the polymer, that we have throughout this thesis referred to as "PHC" after the process of "work up". Note that the dark green color changed after washing with dilute HCl (aq) and essentially the same color (i.e., a similar brown color) was seen for that polymer, as for the "PHC" obtained when acetonitrile was used. I suggest that the (I guess, a salt) washed out with dilute HCl (aq) for the case of DMF could be analyzed using ICP-MS and/or XPS to determine which elements might contribute to the color (or in any case are washed out by the dilute HCl (aq) and this might provide further insight into how reactions are proceeding. As noted above, I studied many different types of electrodes, but we only get a "good" yield when we use the stainless steel electrodes. There is clearly a contribution to the reaction from material in the electrode. Thus, other types of stainless steel should be used. We used SS-316 that contains Cr, Ni, and Mo, as well of course as iron, and a non-trivial amount of Mn as well. SS- 304 doesn't contain Mo, and other stainless steels have other elemental compositions. The reader can, for example, see the compositions of many stainless steels at:

http://www.atlassteels.com.au/documents/Stainless%20Steel%20Grade%20Composition%20Chart.pdf.

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